



# Piezoelectric Resonance in $\text{KH}_2\text{PO}_4$ Type Crystals Revisited

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Within the framework of proton model with taking into account the piezoelectric interaction with the shear strain  $\varepsilon_6$ , a dynamic dielectric response of  $\text{KD}_2\text{PO}_4$  type ferroelectrics is considered. An expression for the piezoelectric resonance frequencies of the rectangular thin plate of the crystal cut in the (001) plane is obtained.

**Key words:** *ferroelectrics, piezoelectric resonance.*

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## 1. Introduction

In our previous paper [ 1] we explored the dynamic dielectric response of square thin plates cut from the  $\text{KH}_2\text{PO}_4$  family ferroelectric crystals in the planes (001), perpendicular to the axis of spontaneous polarization. Using the proposed modification of the proton ordering model [ 2] that includes the piezoelectric coupling with the shear strain  $\varepsilon_6$ , within the framework of the Glauber approach [ 3] and the four-particle cluster approximation, we obtained an expression for the dynamic dielectric permittivity of a crystal, which that takes into account the dynamics of the shear strain  $\varepsilon_6$ . In the low-frequency limit this expression coincided with the static permittivity of a mechanically free crystal, whereas in the microwave region it coincided with the dynamic permittivity of a clamped crystal, exhibiting a relaxational dispersion.

In the intermediate region, the obtained permittivity had numerous peaks associated with the piezoelectric resonances. It should, however, be mentioned that while solving the partial differential equations for the strain in [ 1], the boundary conditions were not set correctly. Instead of demanding that the entire edges of the plate were mechanically free, we considered the plate free only at its vertices. It resulted in the underestimated values of the resonant frequencies. In the present paper we shall correct this error.

We shall not repeat here the details of the previous calculations, which were correct. The system Hamiltonian, most of the used notations, as well as derivation of the dynamic dielectric permittivity of a clamped crystal (the pseudospin subsystem dynamics), can be found in [ 1].

## 2. Calculations

We shall consider vibrations of a thin  $L_x \times L_y$  rectangular plate of a  $\text{KD}_2\text{PO}_4$  crystal, cut in the (001) plane, induced by time-dependent electric field  $E_{3t} = E_3 e^{i\omega t}$ . In the ferroelectric phase this field, in addition to the shear strain  $\varepsilon_6$ , induces also the diagonal components of the strain tensor  $\varepsilon_i$ , but for the sake of simplicity we shall neglect them.

Dynamics of pseudospin subsystem will be considered in the spirit of the stochastic Glauber model [ 3], using the four-particle cluster approximation. The system of equations for the time-

dependent deuteron (pseudospin) distribution functions is

$$-\alpha \frac{d}{dt} \langle \prod_f \sigma_{qf} \rangle = \sum_{f'} \left\{ \langle \prod_f \sigma_{qf} \left[ 1 - \sigma_{qf'} \tanh \frac{1}{2} \beta \varepsilon_{qf'}^z(t) \right] \rangle \right\}, \quad (1)$$

where  $\varepsilon_{qf'}^z(t)$  is the local field acting on the  $f'$ th deuteron in the  $q$ th cell, which can be found from the system Hamiltonian (see [1]);  $\alpha$  is the parameter setting the time scale of the dynamic processes in the pseudospin subsystem.

Taking into account the symmetry of the distribution functions

$$\begin{aligned} \eta^{(1)z} &= \langle \sigma_{q1} \rangle = \langle \sigma_{q2} \rangle = \langle \sigma_{q3} \rangle = \langle \sigma_{q4} \rangle, \\ \eta^{(3)z} &= \langle \sigma_{q1} \sigma_{q2} \sigma_{q3} \rangle = \langle \sigma_{q1} \sigma_{q3} \sigma_{q4} \rangle = \langle \sigma_{q1} \sigma_{q2} \sigma_{q4} \rangle = \langle \sigma_{q2} \sigma_{q3} \sigma_{q4} \rangle, \\ \eta_1^{(2)z} &= \langle \sigma_{q2} \sigma_{q3} \rangle = \langle \sigma_{q1} \sigma_{q4} \rangle, \quad \eta_2^{(2)z} = \langle \sigma_{q1} \sigma_{q2} \rangle = \langle \sigma_{q3} \sigma_{q4} \rangle, \quad \eta_3^{(2)z} = \langle \sigma_{q1} \sigma_{q3} \rangle = \langle \sigma_{q2} \sigma_{q4} \rangle, \end{aligned} \quad (2)$$

from (1), we obtain a closed system of equations for the time-dependent single-particle, pair, and three-particle deuteron distribution functions

$$\alpha \frac{d}{dt} \begin{pmatrix} \eta^{(1)z} \\ \eta^{(3)z} \\ \eta_1^{(2)z} \\ \eta_2^{(2)z} \\ \eta_3^{(2)z} \end{pmatrix} = \begin{pmatrix} \bar{c}_{11} & \bar{c}_{12} & \bar{c}_{13} & \bar{c}_{14} & \bar{c}_{15} \\ \bar{c}_{21} & \bar{c}_{22} & \bar{c}_{23} & \bar{c}_{24} & \bar{c}_{25} \\ \bar{c}_{31} & \bar{c}_{32} & \bar{c}_{33} & \bar{c}_{34} & \bar{c}_{35} \\ \bar{c}_{41} & \bar{c}_{42} & \bar{c}_{43} & \bar{c}_{44} & \bar{c}_{45} \\ \bar{c}_{51} & \bar{c}_{52} & \bar{c}_{53} & \bar{c}_{54} & \bar{c}_{55} \end{pmatrix} \begin{pmatrix} \eta^{(1)z} \\ \eta^{(3)z} \\ \eta_1^{(2)z} \\ \eta_2^{(2)z} \\ \eta_3^{(2)z} \end{pmatrix} + \begin{pmatrix} \bar{c}_1 \\ \bar{c}_2 \\ \bar{c}_3 \\ \bar{c}_4 \\ \bar{c}_5 \end{pmatrix}. \quad (3)$$

The used here notations can be found in [1].

Dynamics of the deformational processes in  $\text{KD}_2\text{PO}_4$  is described using classical Newtonian equations of motion of an elementary volume

$$\rho \frac{\partial^2 u_i}{\partial t^2} = \sum_k \frac{\partial \sigma_{ik}}{\partial x_k}, \quad (4)$$

where  $\rho$  is the crystal density,  $u_i$  are the displacements of the elementary volume along the axis  $x_i$ ,  $\sigma_{ik}$  is the mechanical stress. The shear strain  $\varepsilon_6$  is determined by the displacements  $u_1$  and  $u_2$

$$\varepsilon_6 = 2\varepsilon_{xy} = \frac{\partial u_1}{\partial y} + \frac{\partial u_2}{\partial x}.$$

The expression for the shear stress  $\sigma_{xy} = \sigma_6$ , being the function of  $\eta^{(1)z}$ ,  $E_3$ , and  $\varepsilon_6$ , is found from the constitutive equations derived in [1].

At small deviations from the equilibrium we can separate in the systems (3) and (4) the static and time-dependent parts, presenting the dynamic variables as sums of the equilibrium values and of their fluctuational deviations

$$\begin{aligned} \eta^{(1)} &= \tilde{\eta}^{(1)} + \eta_t^{(1)}, \quad \eta^{(3)} = \tilde{\eta}^{(3)} + \eta_t^{(3)}, \quad \eta_i^{(2)} = \tilde{\eta}_i^{(2)} + \eta_t^{(2)}, \quad (i = 1, 2, 3), \\ \varepsilon_6 &= \tilde{\varepsilon}_6 + \varepsilon_{6t}, \quad u_{1,2} = \tilde{u}_{1,2} + u_{1,2t}. \end{aligned} \quad (5)$$

The fluctuational parts are assumed to be in the form of harmonic waves

$$\begin{aligned} \eta_t^{(1)} &= \eta^{(1)}(x, y) e^{i\omega t}, \quad \eta_t^{(3)} = \eta^{(3)}(x, y) e^{i\omega t}, \dots \\ u_{1t} &= u_1(y) e^{i\omega t}, \quad u_{2t} = u_2(x) e^{i\omega t}, \quad \varepsilon_{6t} = \varepsilon_6(x, y) e^{i\omega t}. \end{aligned}$$

The fluctuational part of (3) is reduced to the system of linear first-order differential equations with constant coefficients, solving which we get

$$\begin{aligned} \eta^{(1)}(x, y) &= \frac{\beta \mu_3}{2} F^{(1)}(\alpha \omega) E_3 + \left[ -\beta \psi_6 F^{(1)}(\alpha \omega) + \right. \\ &\quad \left. + \beta \delta_{s6} F_s^{(1)}(\alpha \omega) - \beta \delta_{a6} F_a^{(1)}(\alpha \omega) + \beta \delta_{16} F_1^{(1)}(\alpha \omega) \right] \varepsilon_6(x, y), \end{aligned} \quad (6)$$

the notations introduced here can be found in [ 1].

Equations (4) reduce to

$$\frac{\partial^2 u_1}{\partial y^2} + k_6^2 u_1 = 0, \quad \frac{\partial^2 u_2}{\partial x^2} + k_6^2 u_2 = 0, \quad (7)$$

where  $k_6$  is the wavenumber

$$k_6 = \frac{\omega \sqrt{\rho}}{\sqrt{c_{66}^E(\alpha\omega)}}, \quad (8)$$

and

$$\begin{aligned} c_{66}^E(\alpha\omega) = & c_{66}^{E0} + \frac{4\beta\psi_6}{vD_6}f_6 + \frac{2\beta}{vD_6^2}(-\delta_{s6}M_{s6} + \delta_{16}M_{16} + \delta_{a6}M_{a6})^2 + \\ & + \frac{4\beta\psi_6}{v} \left[ -\psi_6 F^{(1)}(\alpha\omega) + \delta_{s6} F_s^{(1)}(\alpha\omega) + \delta_{16} F_1^{(1)}(\alpha\omega) - \delta_{a6} F_a^{(1)}(\alpha\omega) \right] - \\ & - \frac{4\varphi_3 f_6}{vD_6} \beta \left[ -\psi_6 F^{(1)}(\alpha\omega) + \delta_{s6} F_s^{(1)}(\alpha\omega) + \delta_{16} F_1^{(1)}(\alpha\omega) - \delta_{a6} F_a^{(1)}(\alpha\omega) \right] - \\ & - \frac{2\beta}{vD_6} \left[ \delta_{s6}^2 \cosh(2\tilde{z} + \beta\delta_{s6}\tilde{\varepsilon}_6) + 4b\delta_{16}^2 \cosh(\tilde{z} - \beta\delta_{16}\tilde{\varepsilon}_6) + \delta_{a6}^2 2a \cosh \beta\delta_{a6}\tilde{\varepsilon}_6 \right]. \end{aligned} \quad (9)$$

Differentiating the first and second equations of (7) with respect to  $y$  and  $x$ , correspondingly, remembering that we neglect the diagonal strains  $\varepsilon_1 = \partial u_1 / \partial x$  and  $\varepsilon_2 = \partial u_1 / \partial y$ , and adding the two obtained equations, we arrive at the single equation for the strain  $\varepsilon_6$

$$\frac{\partial^2 \varepsilon_6(x, y)}{\partial x^2} + \frac{\partial^2 \varepsilon_6(x, y)}{\partial y^2} + k_6^2 \varepsilon_6(x, y) = 0. \quad (10)$$

Boundary conditions for  $\varepsilon_6(x, y)$  follow from the assumption that the crystal is simply supported, that is, it is traction free at its edges (at  $x = 0$ ,  $x = L_x$ ,  $y = 0$ ,  $y = L_y$ , to be denoted as  $\Sigma$ )

$$\sigma_6|_{\Sigma} = 0. \quad (11)$$

In our previous consideration [ 1] this condition was fulfilled at the corners of the crystal plate only, not at all its edges. Substituting (11) into the constitutive relations, we obtain the explicit boundary conditions for the strains in the following form

$$\varepsilon_6|_{\Sigma} \equiv \varepsilon_{i0} = \frac{e_{36}(\alpha\omega)}{c_{66}^E(\alpha\omega)} E_3, \quad (12)$$

where

$$e_{36}(\alpha\omega) = e_{36}^0 + \frac{\beta\mu_3}{v} \left[ -\psi_6 F^{(1)}(\alpha\omega) + \delta_{s6} F_s^{(1)}(\alpha\omega) + \delta_{16} F_1^{(1)}(\alpha\omega) - \delta_{a6} F_a^{(1)}(\alpha\omega) \right]. \quad (13)$$

Solution of (8) with the boundary conditions (12) is

$$\varepsilon_6(x, y) = \varepsilon_{60} + \varepsilon_{60} \sum_{k,l=0}^{\infty} \frac{16}{(2k+1)(2l+1)\pi^2} \frac{\omega^2}{(\omega_{kl}^0)^2 - \omega^2} \sin \frac{\pi(2k+1)x}{L_x} \sin \frac{\pi(2l+1)y}{L_y}, \quad (14)$$

with  $\omega_{kl}^0$  given by

$$\omega_{kl}^0 = \sqrt{\frac{\tilde{c}_{66}^E(\omega_{kl}^0)\pi^2}{\rho} \left[ \frac{(2k+1)^2}{L_x^2} + \frac{(2l+1)^2}{L_y^2} \right]}. \quad (15)$$

Using the expression, relating polarization  $P_3$  to the order parameter  $\eta^{(1)}$  and strain  $\varepsilon_6$  (see [ 1]), we find that

$$P_3(x, y, t) = P_3(x, y) e^{i\omega t}, \quad (16)$$

where

$$P_3(x, y) = e_{36}(\alpha\omega)\varepsilon_6(x, y) + \chi_{33}^\varepsilon(\alpha\omega)E_3,$$

and

$$\chi_{33}^\varepsilon(\alpha\omega) = \chi_{33}^{\varepsilon_0} + \frac{\beta\mu_3^2}{2v}F^{(1)}(\alpha\omega).$$

is the dynamic dielectric susceptibility of a clamped crystal.

Now we can calculate the dynamic dielectric susceptibility of a free crystal  $\chi_{33}^\sigma(\alpha\omega)$

$$\chi_{33}^\sigma(\alpha\omega) = \frac{1}{L_x L_y} \frac{\partial}{\partial E_3} \int_0^{L_x} dx \int_0^{L_y} dy P_3(x, y). \quad (17)$$

From (14), we find that

$$\frac{1}{L_x L_y} \int_0^{L_x} dx \int_0^{L_y} dy \varepsilon_6(x, y) = R_6(\omega) \frac{e_{36}(\alpha\omega)}{c_{66}^E(\alpha\omega)} E_3, \quad (18)$$

where

$$R_6(\omega) = 1 + \sum_{k,l=0}^{\infty} \frac{64}{(2k+1)^2(2l+1)^2\pi^4} \frac{\omega^2}{(\omega_{kl}^0)^2 - \omega^2}.$$

Finally the dynamic dielectric susceptibility is

$$\chi_{11}^\sigma(\omega) = \chi_{11}^\varepsilon(\omega) + R_6(\omega) \frac{e_{36}^2(\alpha\omega)}{c_{66}^E(\alpha\omega)}. \quad (19)$$

In the static limit ( $\omega \rightarrow 0$ ,  $R_6(\omega) \rightarrow 1$ ) from (19) we obtain the static susceptibility of a free crystal [2]; in the high frequency limit ( $\sum_{k,l=0}^{\infty} 64/[(2k+1)^2(2l+1)^2\pi^4] = 1$ , and  $R_6(\omega) \rightarrow 0$ ) we get a dynamic susceptibility of a mechanically clamped crystal, exhibiting relaxational dispersion in the microwave region. Thus, eq. (19) explicitly describes the effect of crystal clamping by high-frequency electric field.

In the intermediate frequency region, the susceptibility has a resonance dispersion with numerous peaks at frequencies where  $\text{Re}[R_6(\omega)] \rightarrow \infty$ . Frequency variation of  $c_{66}^E(\alpha\omega)$  is perceptible only in the region of the microwave dispersion of the dielectric susceptibility. Below this region  $\tilde{c}_{66}^E(\alpha\omega)$  is practically frequency independent and coincides with the static elastic constant  $c_{66}^E$ . Since the resonance frequencies are expected to be in the  $10^4 - 10^7$  Hz range, depending on temperature and sample dimensions, we can neglect the frequency dependence of  $c_{66}^E(\alpha\omega)$  (9) and reduce the equation for the resonance frequencies (15) to an explicit expression by putting in it  $c_{66}^E(\alpha\omega) \rightarrow c_{66}^E$ .

Comparing (15) to the expression obtained previously [1] for a square  $L \times L$  plate cut in the (001) plane

$$\omega_k = \frac{\pi(2k+1)}{L} \sqrt{\frac{c_{66}^E(\omega_k)}{\rho}},$$

we can see that the incorrectly set boundary conditions [1] led to the  $\sqrt{2}$  times smaller lowest resonance frequency than the correct one. However, the low and high frequency limits of the susceptibility (the static value and the clamped values with the relaxational dispersion in the microwave region) were correct.

### 3. Conclusions

Within the proton ordering model with taking into account the shear strain  $\varepsilon_6$  we explored a dynamic response of the  $\text{KD}_2\text{PO}_4$  type crystals to an external harmonic electric field  $E_3$ . Dynamics

of the pseudospin subsystem is described within the stochastic Glauber approach. Dynamics of the strain  $\varepsilon_6$  is obtained from the Newtonian equations of motion of an elementary volume, with taking into account the relations between the order parameter of the pseudospin subsystem and the strain in the static limit. A corrected expression for the piezoelectric resonance frequencies of the rectangular thin plates of these crystals cut in the (001) plane is obtained.

The ultimate goal of the present studies is will be to generalize the obtained expression for the dynamic permittivity the case of the mixed  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{PO}_4$  type systems, exhibiting the proton glass properties, in order to explore the dynamic dielectric response. It is known that, just like their pure constituents, these mixed systems are piezoelectric, and their dynamic dielectric permittivity has a piezoelectric resonance dispersion [ 4]. As our preliminary calculations show, the experimentally obtained resonant frequencies of such mixed crystals [ 5] are well described by the obtained here expression for the resonant frequencies, provided that the corresponding elastic constant  $c_{66}^E$  of such a system is known.

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